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Mayer and virial series at low temperature

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Abstract

We analyze the Mayer pressure-activity and virial pressure-density series for a classical system of particles in continuous configuration space at low temperature. Particles interact via a finite range potential with an attractive tail. We propose physical interpretations of the Mayer and virial series' radius of convergence, valid independently of the question of phase transition: the Mayer radius corresponds to a fast increase from very small to finite density, and the virial radius corresponds to a cross-over from monatomic to polyatomic gas. Our results have consequences for the search of a low density, low temperature solid-gas phase transition, consistent with the Lee-Yang theorem for lattice gases and with the continuum Widom-Rowlinson model.

1 Introduction

The present work started from a seeming contradiction between results on cluster size distributions at low temperature and low density [9] and predictions from the Mayer activity expansions. It turned out that not only is there no contradiction, but moreover the interplay between the two different approaches considerably helps the physical interpretation of the classical expansions.

The seeming contradiction is the following. Consider a classical system of particles, interacting via a stable potential with an attractive tail. As is well-known from the theory of Mayer expansions (see e.g., the classical textbook [16]), at low density, the system behaves approximately like an ideal gas, suggesting that particles move more or less independently and are typically far from each other. But [9] showed that when both the density and temperature are small, there can be regimes where particles form small compounds – the system could behave, for example, like a diatomic gas. Such a behavior is, in fact, well established for quantum Coulomb systems [2, 5, 6].

In order to fit both pictures together, we investigate the temperature dependence of the Mayer and virial series. The temperature dependence confirms the intuitive relation between Mayer's series and Frenkel-Band theory of physical clusters, as exposed in [7, Chapter 5]: the Mayer series $\beta p = \sum b_k z^k$ looks like the pressure of an ideal mixture of size k components with respective activities $b_k z^k$. But unlike physical activities, the coefficients b_k can be negative. The gas is therefore, at best, an *exact* ideal mixture of *fictitious* objects, "*mathematical*" clusters. On the other hand, at low density, it is tempting to consider the system as an *approximately* ideal mixture of "*physical*" clusters, groups of particles close in configuration space.

Each physical cluster comes with a partition function over internal degrees of freedom. At low temperatures, it is natural to approximate the internal partition function as $\exp(-\beta E_k)$, with E_k

a ground state energy, and we expect

$$\beta p \approx \sum_k z^k \exp(-\beta E_k). \tag{1}$$

We prove that at low temperatures, the Mayer series coefficients $b_k(\beta)$ indeed behave as $\exp(-\beta(E_k + o(1)))$, so that the approximation described above matches the exact Mayer series. As a consequence, we can easily understand the formation of compounds: if $\beta \to \infty$ at fixed chemical potential μ, we have to maximize $(k\mu - E_k)$ in order to see which k gives the dominant contribution. In particular, even when the Mayer series converges, at low temperatures the main contribution does not necessarily come from $k = 1$.

With the approximate formula (1) in mind, we show several results on Mayer and virial series and low temperature statistical physics, stated in Sect. 3; the proofs are given in Sects 4–7. We hope to convince the reader that the radius of convergence of both the pressure-activity and pressure-density series have physical interpretations. They do not necessarily correspond sharp phase transitions, and may very well be determined by singularities off the positive axis; nevertheless, they reflect changes in low-temperature physical behavior. This is formally analogous to resonances in quantum mechanics, when Green's function singularities off the real axis do not qualify as eigenvalues, but can nonetheless affect the system's behavior.

2 Setting

We are interested in the statistical mechanics for a classical system of particles, in continuous configuration space, interacting via a pair potential $v(|x-y|)$. Thus let $v : [0,\infty) \to \mathbb{R} \cup \{\infty\}$ and

$$U(x_1, \dots, x_N) := \sum_{1 \le i < j \le N} v(|x_i - x_j|)$$

be the energy of a configuration of N particles $x_1, \dots, x_N \in \mathbb{R}^d$. We assume that the energy is *stable*, i.e., there is a constant $B \ge 0$ such that

$$\forall N \in \mathbb{N},\ \forall (x_1, \dots, x_N) \in (\mathbb{R}^d)^N :\ U(x_1, \dots, x_N) \ge -BN. \tag{2}$$

In addition, we assume that the pair potential has finite range, i.e., v has compact support. For a given inverse temperature $\beta > 0$ and $\Lambda \subset \mathbb{R}^d$, the canonical partition function is

$$Z_\Lambda(\beta, N) := \frac{1}{N!} \int_{\Lambda^N} e^{-\beta U(x_1, \dots, x_N)} \mathrm{d}x_1 \cdots \mathrm{d}x_N,$$

and the free energy per unit volume is

$$f(\beta, \rho) := -\lim \frac{1}{\beta |\Lambda|} \log Z_\Lambda(\beta, N).$$

The limit is along $N \to \infty$, $\Lambda = [0, L]^d$ with $L \to \infty$, $N/L^d \to \rho > 0$. It is well-known that if the potential has no hard core ($r_{\mathrm{hc}} = 0$), the limit exists and is finite for all $\rho > 0$; if the potential has a hard core, then for a suitable number $\rho_{\mathrm{cp}} > 0$ (the *close-packing density*), the limit is finite for $\rho < \rho_{\mathrm{cp}}$, and infinite for $\rho > \rho_{\mathrm{cp}}$. Moreover the free energy $f(\beta, \rho)$ is a convex function of the density ρ.

The pressure at inverse temperature β and chemical potential $\mu \in \mathbb{R}$ is

$$p(\beta, \mu) := \sup_{0<\rho<\rho_{\mathrm{cp}}} \big(\rho\mu - f(\beta, \rho)\big). \tag{3}$$

We call $\rho(\beta, \mu)$ the maximizer in the previous relation, if it is unique. Because of convexity, the density $\rho(\beta, \mu)$ is an increasing function of the chemical potential μ.

At fixed temperature, for sufficiently negative chemical potential, the pressure is an analytic function of the chemical potential, with expansion

$$\beta p(\beta, \mu) = z + \sum_{n\geq 2} b_n(\beta) z^n, \qquad z = \exp(\beta\mu), \tag{4}$$

the *Mayer series*, and the density is given by

$$\rho(\beta, \mu) = z + \sum_{n=2}^{\infty} n b_n(\beta) z^n.$$

Similarly, at low density, the free energy is strictly convex and analytic with expansion

$$\beta f(\beta, \rho) = \rho(\log \rho - 1) - \sum_{n\geq 2} d_n(\beta)\rho^n. \tag{5}$$

Eq. (3) gives, for μ negative enough,

$$\beta p(\beta, \mu) = \rho - \sum_{n\geq 2} (n-1) d_n(\beta)\rho^n, \quad \rho = \rho(\beta, \mu), \tag{6}$$

the *virial series*. We would like to know how large z, or ρ, can be in those equations, and define

$$R^{\mathsf{May}}(\beta) := \sup\big\{\rho > 0 \mid \text{Eq. (4) is true with absolutely convergent series}\big\},$$
$$R^{\mathsf{vir}}(\beta) := \sup\big\{\rho > 0 \mid \text{Eq. (5) is true with absolutely convergent series}\big\}.$$

In principle, $R^{\mathsf{May}}(\beta)$ and $R^{\mathsf{vir}}(\beta)$ can be smaller than the radius of convergence of the corresponding series. For non-negative potentials, however, it is known [10] that the domains of convergence coincide with the domain of equality of Eqs. (4), (5), and (6), so that in this case $R^{\mathsf{May}}(\beta)$ and $R^{\mathsf{vir}}(\beta)$ are exactly equal to the radius of convergence.

Furthermore we define

$$\mu_{\mathrm{sat}}(\beta) := \sup\{\tilde{\mu} \in \mathbb{R} \mid p(\beta, \mu) \text{ is analytic in } \mu < \tilde{\mu}\},$$
$$\rho_{\mathrm{sat}}(\beta) := \sup\{R \in (0, \rho_{\mathrm{cp}}) \mid f(\beta, \rho) \text{ is analytic in } 0 < \rho < R\}.$$

the chemical potential and density at the onset of condensation, i.e., the quantities associated with saturated gas. In the absence of a phase transition – for example, in one dimension –, $\mu_{\mathrm{sat}}(\beta) = \rho_{\mathrm{sat}}(\beta) = \infty$. Another quantity of interest is

$$\rho^{\mathsf{May}}(\beta) := \sup\{\rho(\beta, \mu) \mid \exp(\beta\mu) < R^{\mathsf{May}}(\beta)\}.$$

We have the general bounds

$$\beta^{-1} \log R^{\mathsf{May}}(\beta) \leq \mu_{\mathrm{sat}}(\beta), \qquad \max\Big(R^{\mathsf{vir}}(\beta), \rho^{\mathsf{May}}(\beta)\Big) \leq \rho_{\mathrm{sat}}(\beta).$$

With these notations, we can ask:

> **Question:** When are the previous inequalities strict? When they are strict, is it nevertheless possible to give physical meaning to R^{May} and R^{vir}, even though in this case R^{May} and R^{vir} do not correspond to phase transitions (i.e., points of non-analyticity) ?

The main goal of this article is to convince the reader that the answer to the second question should be yes; moreover, in the presence of a phase transition for attractive potentials, the inequalites should be approximate equalities, in a sense specified in the Corollary 3.3 and the Conjectures 3.4 and 3.9 below.

We conclude this section with a description of the convergence criterium for the Mayer series that we shall use. Let

$$E_N := \inf_{x_1,\ldots,x_N \in (\mathbb{R}^d)^N} U(x_1,\ldots,x_N), \quad E_1 = 0, \tag{7}$$

be the ground state energy for N particles (without any volume constraint), and

$$e_\infty := \inf_{N\in\mathbb{N}} \frac{E_N}{N} = \lim_{N\to\infty} \frac{E_N}{N} \leq 0 \tag{8}$$

(note that (E_N) is subadditive). The stability assumption on the pair potential ensures that $e_\infty > -\infty$, and Eq. (2) holds with $B = -e_\infty$ as optimal constant. We shall make repeated use of the following Theorem, which is a direct consequence of from [13, Theorem 2.1], see also [1] for integrable potentials (without hard core).

Theorem 2.1 (Mayer series estimates [13]). *Let $v(|x-y|)$, be a stable pair interaction potential. Suppose that $||\bar v||_1 := \int_{\mathbb{R}^d} |\bar v(|x|)|\mathrm{d}x < \infty$ where $\bar v(r) = v(r)$ if $v(r) < \infty$, and $\bar v(r) = 1$ if $v(r) = \infty$. If $z \geq 0$ satisfies*

$$\beta z e^{-\beta e_\infty} \int_{\mathbb{R}^d} |\bar v(x)|\mathrm{d}x \leq 1/e, \tag{9}$$

then $z \leq R^{\mathsf{May}}(\beta)$, and

$$\sum_{n\geq 2} n|b_n(\beta)|z^{n-1} \leq (e-1)e^{-\beta e_\infty}. \tag{10}$$

As an immediate consequence, we note that

$$\liminf_{\beta\to\infty} \mu_{\mathrm{sat}}(\beta) \geq \liminf_{\beta\to\infty} \beta^{-1}\log R^{\mathsf{May}}(\beta) \geq e_\infty. \tag{11}$$

Therefore every chemical potential $\mu < e_\infty$, as $\beta \to \infty$, eventually falls into the gas phase.

3 Results and conjectures

Our standard assumptions on the potential are the following:

Assumption 1 (Minimal assumptions)**.** $v : [0, \infty) \to \mathbb{R} \cup \{\infty\}$ satisfies the following assumptions:

- The energy is stable in the sense of Eq. (2).
- v is everywhere finite except possibly for a hard core: there is a $r_{\mathrm{hc}} \geq 0$ such that $v(r) = \infty$ for $r < r_{\mathrm{hc}}$ and $v(r) > \infty$ for $r > r_{\mathrm{hc}}$.
- v has compact support, $b := \sup\{r > 0 \mid v(r) \neq 0\} < \infty$.
- v is continuous in $[r_{\mathrm{hc}}, \infty)$.
- v has an attractive tail: for suitable $\delta > 0$ and all $x \in (b - \delta, b)$, $v(r) < 0$.

Note that we allow for $v(r_{\mathrm{hc}}) < \infty$, which is relevant for Radin's soft disk potential [15].

The previous assumptions will be enough when working in the low density gas phase. For results that hold all the way up into a finite density region, we will make additional assumptions. We refer to every minimizer $(x_1, \ldots, x_N) \in (\mathbb{R}^d)^N$ of $U(x_1, \ldots, x_N)$ as a N-particle *ground state*. Note that the attractive tail favors configurations where particles stick together.

Assumption 2 (Ground state geometry and Hölder continuity)**.** For suitable $a > 0$, $r_0 > 0$, and every $N \in \mathbb{N}$, there is a N-particle ground state $(x_1, \ldots, x_N) \in (\mathbb{R}^d)^N$ such that

- the interparticle distance is lower-bounded by r_0: for all $i \neq j$, $|x_i - x_j| \geq r_0$;
- the ground state fits into a cube of volume ka^d: $x_1, \ldots, x_N \in [0, k^{1/d}a]^d$.

Moreover $v(r)$ is uniformly Hölder continuous in $[r_0, \infty)$.

The simplest example, in dimension two, of a potential satisfying Assumptions 1 and 2 is Radin's soft disk potential [15]. More general potential classes, again in dimension two, are given in [19].

Assumption 2 is enough to ensure that various limits can be interchanged. In particular, if

$$e(\rho) := \lim_{\beta \to \infty} f(\beta, \rho)$$

is the ground state energy per unit volume at density ρ, then

$$e_\infty = \min_{0 < \rho < \rho_{\mathrm{cp}}} \frac{e(\rho)}{\rho}.$$

Moreover $e(\rho)/\rho$ has a minimizer $\rho^* \leq 1/a^d$, i.e., the ground state has a finite preferred density. In [15, 19], ρ^* is the density of particles in a simple hexagonal lattice.

Our first result is about the low-temperature behavior of the Mayer coefficients and should be contrasted with the alternating sign property for non-negative potentials [16, Chapter 4]. Recall the ground state energies E_N from Eq. (7).

Theorem 3.1 (Mayer coefficients at low temperature)**.** *Suppose that v satisfies Assumption 1. Then, for every fixed k, as $\beta \to \infty$, $b_k(\beta)$ is eventually positive, and*

$$\lim_{\beta\to\infty} \beta^{-1} \log b_k(\beta) = -E_k. \tag{12}$$

Thus we may think of the Mayer series as

$$\beta p \approx \sum_k z^k \exp(-\beta E_k). \tag{13}$$

The subsequent results are best understood with the approximate formula (13) in mind. We should stress that the approximation (13) can be derived without using Mayer expansions, see [5] for a quantum Coulomb systems result. Direct proofs are, in fact, much more instructive from a physical point of view; therefore Theorem 3.1 should be seen as a verification of the consistency of the Mayer series with the approximation (13).

The next theorem builds upon a low temperature, low density result from [9] which we briefly recall. Suppose that v satisfies Assumptions 1 and 2. Then, for suitable $\beta_0, \rho_0, C_0 > 0$ and all $\beta \geq \beta_0$ and $\rho < \rho_0$,

$$\Bigl| f(\beta,\rho) - \rho \inf_{k\in\mathbb{N}} \frac{E_k + \beta^{-1}\log\rho}{k} \Bigr| \leq C_0 \rho \beta^{-1} \log \beta. \tag{14}$$

The density ρ_0 can be chosen of the order of the preferred ground state density, $1/a^d$, with a as in Assumption 2, see Appendix B. We will also need the auxiliary quantity

$$\nu^* := \inf_{k\in\mathbb{N}} (E_k - k e_\infty) \geq 0.$$

For potentials with an attractive tail, $\nu^* > 0$ [9].

Theorem 3.2 (Density increase around $\mu = e_\infty$)**.** *Suppose that v satisfies Assumptions 1 and 2, and that v is integrable in $|x| > r_{\mathrm{hc}}$. Let C_0, β_0 and ρ_0 be as for Eq.* (14)*. Then:*

- *For every $C > C_0$,suitable $\beta_C \geq \beta_0 > 0$, and all $\beta \geq \beta_C$,*

$$\mu \geq e_\infty + C\beta^{-1}\log\beta \;\Rightarrow\; \rho(\beta,\mu) \geq \frac{C - C_0}{C + C_0}\rho_0.$$

- *For every $C > 1$, all $n \in \mathbb{N}$, suitable $\beta(n,C)$ and and all $\beta \geq \beta(n,C)$,*

$$\mu \leq e_\infty - C\beta^{-1}\log\beta \;\Rightarrow\; \rho(\beta,\mu) \leq \beta^{-n}.$$

In particular, for every fixed $\mu > e_\infty$, as $\beta \to \infty$, the density is bounded away from zero, while for $\mu < e_\infty$, it vanishes exponentially fast (Eq. (15) anticipates on Theorem 3.2):

$$\begin{aligned} \mu > e_\infty &: \liminf_{\beta\to\infty} \rho(\beta,\mu) \geq \rho_0 > 0. \\ \mu < e_\infty &: \qquad\quad \rho(\beta,\mu) = O(e^{-\beta\nu^*}). \end{aligned} \tag{15}$$

Remark (Non-negative potentials). When $v \geq 0$, a similar change in the density behavior occurs around $\mu = 0$, as the following two examples illustrate. For an ideal gas in continuum space, $\beta p = z$, $\rho = z$, $e_\infty = 0$. For a lattice gas with no interaction except the hard-core on-site repulsion,

$$\beta p(\beta, \mu) = \log(1 + z), \quad \rho(\beta, \mu) = \frac{z}{1+z}, \quad e_\infty = 0.$$

As $\beta \to \infty$, if $\mu > 0$ is fixed, the density diverges (for the ideal gas) or approaches the maximum density (for the lattice gas). For both the continuum and lattice gas, at fixed $\mu < 0$, the density goes to 0 exponentially fast, but in contrast with the attractive potential case Eq. (15) there is no positive lower bound on the rate of exponential decay, $\nu^* = 0$.

A first consequence is an indication where the low temperature, low density solid-gas transition, if there is any, is located.

Corollary 3.3 (Where to look for a solid-gas transition)**.** Under the assumptions of Theorem 3.2, if $\rho_{\mathrm{sat}}(\beta) \to 0$ as $\beta \to \infty$, then necessarily

$$\mu_{\mathrm{sat}}(\beta) = e_\infty + O(\beta^{-1} \log \beta)$$

as $\beta \to \infty$.

The corollary follows from Theorem 3.2 and the observation that $\mu_{\mathrm{sat}}(\beta) \geq \beta^{-1} \log R^{\mathrm{May}}(\beta)$, combined with the convergence criterion from Eq. (9).

Remark (Lee-Yang theorem). For a lattice gas on $\mathbb{Z}^d$ with attractive pair interactions $v(x-y) \leq 0$, the Lee-Yang theorem [16, Theorem 5.1.3] says that if there is a phase transition, then it must be at

$$\exp\Big(\beta\mu - \frac{1}{2}\sum_{x\neq 0} \beta v(x)\Big) = 1,$$

equivalently at chemical potential $\mu = (\sum_{x\neq 0} v(x))/2$. The right-hand side of the latter equality is readily identified as e_∞, the ground state energy per particle for the lattice gas. Thus Corollary 3.3 compares well with the Lee-Yang theorem.

Remark (Widom-Rowlinson model). It is instructive to look at a continuum space model for which the existence of a phase transition is known, the *Widom-Rowlinson model* [20], see the review [18]. Consider particles interacting via the energy

$$U_\Lambda(x_1, \ldots, x_N) = \big|\Lambda \cap \cup_{i=1}^N B(x_i, 1)\big| - N\big|B(0,1)\big|$$

wher $B(x,1)$ is the ball of radius 1 centered at x. The interaction is not a sum of pair interactions, but it qualifies nevertheless as an attractive, stable, finite-range interaction. The ground state energy per particle is $e_\infty = -|B(0,1)|$. An equivalent formulation is in terms of a two-species model with hard core repulsion between particles of different type:

$$\sum_{N=0}^\infty \frac{z^N}{N!} \int_{\Lambda^N} e^{-\beta U_\Lambda(\boldsymbol{x})} \mathrm{d}\boldsymbol{x} \\ = e^{-z_2|\Lambda|} \sum_{N_1, N_2 = 0}^\infty \frac{z_1^{N_1}}{N_1!} \frac{z_2^{N_2}}{N_2!} \int_{\Lambda^{N_1}} \int_{\Lambda^{N_2}} \mathbf{1}\big(\mathrm{dist}(\boldsymbol{x}, \boldsymbol{y}) \geq 1\big) \mathrm{d}\boldsymbol{x}\mathrm{d}\boldsymbol{y},$$

provided

$$\beta = z_2, \quad z = z_1 e^{-z_2|B(0,1)|}.$$

It is known [17, 3] that for sufficiently high, equal activities $z_1 = z_2$, the system has a phase transition. In the one-species picture, a phase transition happens at low temperature and activity $z = \beta \exp(-\beta |B(0,1)|)$, or chemical potential

$$\mu = -|B(0,1)| + \beta^{-1} \log \beta = e_\infty + \beta^{-1} \log \beta.$$

Again, this matches Corollary 3.3.

A second consequence of Theorem 3.2 is that, even when there is no phase transition – for example, in one dimension –, there is nevertheless a change in physical behavior around $\mu = e_\infty$: consider the family of curves $\mu \mapsto \rho(\beta, \mu)$ around $\mu = e_\infty$. At $\beta = \infty$, it has a jump of size $\geq \rho_0$. At β large but finite, there could be either a jump, or the curves resemble the occupation numbers of fermions around the Fermi energy. Hence there is either a phase transition, or a fast increase from small to large density.

We would like to propose this as a a physical interpretation to the domain of convergence of the Mayer series, for attractive potentials, based on the following conjecture:

Conjecture 3.4 (Mayer series' radius of convergence)**.** Suppose that v satisfies Assumptions 1 and 2. Then

$$\lim_{\beta \to \infty} \beta^{-1} \log R^{\mathsf{May}}(\beta) = e_\infty. \tag{16}$$

Note that for pair potentials whose finite part is integrable, we have the lower bound Eq. (11) on the liminf. Hence the only part that is open in the previous conjecture is an upper bound on the limsup.

In fact, if we are willing to allow for a minor modification of the definition of $R^{\mathsf{May}}(\beta)$, a rigorous statement can be proven by combining Theorem 3.1 with the bounds from [12]. First recall that the pressure $\beta p_\Lambda(\beta, z)$, defined via the logarithm of the grand-canonical partition function in a finite box $\Lambda = [0, L]^d$, has a Mayer expansion similar to Eq. (4), with volume-dependent radius of convergence $R_\Lambda^{\mathsf{May}}(\beta)$, and $\limsup_{|\Lambda| \to \infty} R_\Lambda^{\mathsf{May}}(\beta) \leq R^{\mathsf{May}}(\beta)$.

Theorem 3.5. *Let the pair interaction satisfy Assumptions 1 and 2. Then, if we let first $|\Lambda| \to \infty$ along cubes, and then $\beta \to \infty$,*

$$\lim_{\beta \to \infty} \limsup_{|\Lambda| \to \infty} \beta^{-1} \log R_\Lambda^{\mathsf{May}}(\beta) = \lim_{\beta \to \infty} \liminf_{|\Lambda| \to \infty} \beta^{-1} \log R_\Lambda^{\mathsf{May}}(\beta) = e_\infty.$$

We are now heading towards similar interpretations for the virial expansion. First, we note that inside the gas phase, there might be "chemical" transitions [8], say, from monatomic to diatomic gas. The next theorem is a grand-canonical version of results from [9] and should be compared to the atomic or molecular limit for quantum Coulomb systems [2, 5, 6]. (See also a a result for the classical one-dimensional two-component plasma [11].)

Theorem 3.6 (Possible cross-overs inside the gas phase)**.** *Suppose that v satisfies Assumption 1 and that v is integrable in $|x| > r_{\mathrm{hc}}$. Then for every fixed $\mu < e_\infty$,*

$$\lim_{\beta \to \infty} \beta^{-1} \log \rho(\beta, \mu) = -\inf_{k \geq 1} (E_k - k\mu) < -\nu^* < 0. \tag{17}$$

If in addition $\inf(E_k - k\mu)_{k\in\mathbb{N}}$ *has a unique minimizer* $k(\mu) \in \mathbb{N}$*, then as* $\beta \to \infty$*,*

$$\beta p(\beta,\mu) = \frac{\rho(\beta,\mu)}{k(\mu)}\,(1+o(1)). \tag{18}$$

The interpretation is that the gas is, approximately, an ideal gas of molecules consisting of $k(\mu)$ particles each, with effective activity $z^k \exp(-\beta E_k)$, see also Eq. (13).

The auxiliary variational problem $E_k - k\mu \stackrel{!}{=} \min$ and its relation with the minimization problem $(E_k + \beta^{-1}\log\rho)/k \stackrel{!}{=} \min$ from Eq. (14) are discussed in more detail in Appendix A. Of particular interest here is the following: let

$$\mu_1 := \inf_{k\in\mathbb{N}} \frac{E_k}{k-1} \le e_\infty, \quad \nu_1 := -\mu_1 \ge \nu^*.$$

For $\mu < \mu_1$, $E_k - k\mu$ has the unique minimizer $k(\mu) = 1$ and minimum value ν_1. If $\mu_1 < e_\infty$, then $\nu_1 > -e_\infty > \nu^*$ and for every $\mu \in (\mu_1, e_\infty)$, each minimizer of $E_k - k\mu$ is larger or equal to $p \ge 2$, where p is the (unique) integer such that $E_k/(k-1) = \mu_1$.

As a consequence, for sufficiently negative chemical potentials, we observe a monatomic gas ($k(\mu) = 1$). If $\mu_1 = e_\infty$, this is all we see in the gas phase. If $\mu_1 < e_\infty$, as we increase the chemical potential, we observe a transition from monatomic to polyatomic gas before the gas condenses.

The existence of such a transition becomes very natural when we look at a concrete example, taken from [4, Sect. 6]. Consider a pair potential with a hard core and two potential wells, a very deep well at small distances, and a very shallow well at larger distances, separated by a repulsive ($v > 0$) part at intermediate distances. The deep well favors small groups of particles (pairs, triangles or tetraeders, depending on the dimension), arranged at larger distances between them; think of a solid made of molecules instead of atoms. It is natural, then, that the solid forms after atoms gather in molecules. A rigorous statement with a proof of $\nu_1 > \nu^*$ (equivalent to $\mu_1 < e_\infty$), for dimension one, can be found in [4].

This example suggests a relationship between the geometry of ground states and the existence or non-existence of a cross-over inside the gas phase. An interesting open question is, therefore, whether the conditions from [19, 21] ensuring a crystalline ground state with hexagonal lattice (one particle per unit cell) also imply $\mu_1 = e_\infty$. A much weaker result is the following:

Proposition 3.7 (Criterion for the absence of polyatomic gas)**.** *Let* v *be a stable pair interaction with attractive tail.*

1 *If for all* $m, n \in \mathbb{N}$*,*

$$E_{m+n+1} \le E_{m+1} + E_{n+1} \tag{19}$$

then $\mu_1 = e_\infty$*.*

2 *If* $v(r) \le 0$ *for all* $r > r_{\mathrm{hc}}$*, then Eq.* (19) *is true for all* m, n*, and* $\mu_1 = e_\infty$*.*

Eq. (19) should be read with a "gluing" operation in mind: instead of juxtaposing m and n-particle configurations in space, as is done in order to derive the subadditivity $E_{m+n} \leq E_m + E_n$, we glue two configurations with $m+1$ and $n+1$ in one point.

After this excursion into ground states, we back to the virial series.

Theorem 3.8 (Comparison of R^{vir}, ρ^{May}, ρ_{sat} and ν_1)**.** *Suppose that v satisfies Assumptions 1 and 2. Then*

$$\liminf_{\beta\to\infty} \beta^{-1} \log \rho_{\mathrm{sat}}(\beta) \geq \liminf_{\beta\to\infty} \beta^{-1} \log \rho^{\mathsf{May}}(\beta) \geq -\nu^*, \tag{20}$$

$$\liminf_{\beta\to\infty} \beta^{-1} \log R^{\mathsf{vir}}(\beta) \geq -\nu_1. \tag{21}$$

If in addition $\mu_1 < e_\infty$ and $E_k/(k-1)$ has a unique minimizer, then

$$\lim_{\beta\to\infty} \beta^{-1} \log R^{\mathsf{vir}}(\beta) = -\nu_1 < -\nu^*, \tag{22}$$

and $R^{\mathrm{vir}}(\beta) \ll \rho^{\mathsf{May}}(\beta) \leq \rho_{\mathrm{sat}}(\beta)$.

It is natural to think that the radius of convergence of the virial expansion, for attractive potentials, is always determined by the first cross-over, either from monatomic to polyatomic gas, or directly from small density, monatomic gas, to large density.

Conjecture 3.9. For interactions with an attractive tail,

$$\lim_{\beta\to\infty} \beta^{-1} \log \rho^{\mathsf{May}}(\beta) = -\nu^*, \quad \lim_{\beta\to\infty} \beta^{-1} \log R^{\mathsf{vir}}(\beta) = -\nu_1 \leq -\nu^*.$$

If in addition there is a low-density, low-temperature phase transition, i.e., if $\rho_{\mathrm{sat}}(\beta) \to 0$ as $\beta \to \infty$, then

$$\lim_{\beta\to\infty} \beta^{-1} \log \rho_{\mathrm{sat}}(\beta) = -\nu^*.$$

Let us recall that the line $\rho = \exp(-\beta\nu^*)$ has the following physical interpretation, proven in [9]: at densities that are very small but higher than $\exp(-\beta\nu^*)$, particles tend to gather in very large clusters (i.e., groups of particles close in space), even though the system is dilute. At densities smaller than $\exp(-\beta\nu^*)$, particles stay for themselves or form small groups – this is the gas phase discussed above.

Finally, we have partial results on the low-temperature asymptotics of the virial coefficients, to be compared with Theorem 3.1.

Proposition 3.10 (Virial coefficients in the absence of polyatomic gas)**.** *Let v satisfy Assumption 1. Suppose that Eq.* (19) *holds for all $m, n \in \mathbb{N}$. Then $\mu_1 = e_\infty$ and for all $k \geq 2$,*

$$\limsup_{\beta\to\infty} \beta^{-1} \log d_k(\beta) \leq -E_k.$$

If in addtion the inequality (19) *is strict for all $m, n \in \mathbb{N}$, the previous inequality for the limsup becomes an equality for the limit.*

Proposition 3.11 (Virial coefficients in the presence of a monatomic-diatomic transition)**.** *Suppose that v satisfies Assumption 1, and in addition $\mu_1 < e_\infty$ and $E_k/(k-1)$ has the unique minimizer $k=2$. Then for every $k \geq 2$, as $\beta \to \infty$, $d_k(\beta)$ eventually has the sign of $(-1)^{k-1}$, and*

$$\lim_{\beta\to\infty} \beta^{-1} \log\Big((-1)^{k-1} d_k(\beta)\Big) = -(k-1)E_2 > -E_k.$$

In particular, $|d_k(\beta)|/b_k(\beta) \to \infty$ as $\beta \to \infty$.

The natural generalization when $\mu_1 = E_p/(p-1)$ for a unique $p \geq 3$ is

$$d_{1+r(p-1)+q}(\beta) \approx (-1)^{r-1} d_{q+1}(\beta) \exp\big(-\beta r (E_p + o(1)\big),$$

$r \in \mathbb{N}_0,\ q = 0,1,\dots,p-2$. We leave the proof, or disproof, as an open problem, and do not exclude surprises – it is not impossible that additional conditions, in the spirit of Eq. (19), are needed.

4 Mayer coefficients at low temperature

Here we prove Theorem 3.1. We use the usual short-hand $v_{ij} = v(|x_i - x_j|)$, and f_{ij} as in

$$\exp(-\beta v(|x_i - x_j|)) = \exp(-\beta v_{ij}) = 1 + f_{ij}.$$

We recall the expression of the Mayer coefficient: it is known that

$$b_k(\beta) = \frac{1}{k!} \sum_{\gamma \text{ conn.}} \int_{(\mathbb{R}^d)^{k-1}} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}) \mathrm{d}x_2 \cdots \mathrm{d}x_k, \quad x_1 := 0. \tag{23}$$

The sum is over connected, undirected graphs $\gamma = (V,E)$ with vertices $1,\dots,k$, and $\prod_{(ij)\in\gamma}$ is the product over edges $\{i,j\} \in E$, $i<j$ (no self-edges (ii)).

Let us start with a look at the $\beta \to \infty$ behavior for an individual graph. Observing that

$$f_{ij}(\boldsymbol{x}) = \begin{cases} (1+o(1)) \exp(-\beta v_{ij}(\boldsymbol{x})), & v_{ij}(\boldsymbol{x}) < 0, \\ -1 + o(1), & v_{ij}(\boldsymbol{x}) \geq 0, \end{cases}$$

we get

$$\prod_{(ij)\in\gamma} \big| f_{ij}(\boldsymbol{x})\big| = (1+o(1)) \exp\Big(-\beta \sum_{(ij)\in\gamma} v_{ij}(\boldsymbol{x}) \mathbf{1}(v_{ij}(\boldsymbol{x}) < 0)\Big).$$

In the exponent, only negative interactions appear. As a result, we may end up with energies much smaller than the ground state energy, seemingly contradicting Theorem 3.1. The reason is, of course, that there are cancellations between different graphs. In order to get a hold on them, it is convenient to do separate book-keepings for "positive" and "negative" edges. Given $\boldsymbol{x} = (x_1,\dots,x_k)$, we define

$$\mathcal{E}^+(\boldsymbol{x}) := \big\{ \{i,j\} \mid 1 \leq i < j \leq k,\ v_{ij}(\boldsymbol{x}) > 0 \big\}$$
$$\mathcal{E}^-(\boldsymbol{x}) := \big\{ \{i,j\} \mid 1 \leq i < j \leq k,\ v_{ij}(\boldsymbol{x}) < 0 \big\}.$$

and let $\gamma^{\pm}(\boldsymbol{x})$ be the graphs with vertices $1,\dots,k$ and edge sets $\mathcal{E}^{\pm}(\boldsymbol{x})$.

The next simplifying observation is that if the interaction has a finite range $R > 0$, $f_{ij}(\boldsymbol{x})$ vanishes as soon as $|x_i - x_j| > R$. Therefore we define, for $\boldsymbol{x} = (x_1,\dots,x_k)$,

$$\mathcal{E}(\boldsymbol{x}) := \big\{\{i,j\} \mid 1 \le i < j \le k,\ |x_i - x_j| \le R\big\},$$

and let $\gamma(\boldsymbol{x})$ be the graph with vertices $1,\dots,k$ and edge set $\mathcal{E}(\boldsymbol{x})$. We call a configuration $\boldsymbol{x}$ *connected* if the graph $\gamma(\boldsymbol{x})$ is connected, and write $\mathbf{1}_{\mathrm{conn}}(\boldsymbol{x})$ for the corresponding characteristic function. With these notations, for every configuration $\boldsymbol{x}$ and every graph γ,

$$\prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}) \neq 0 \ \Rightarrow\ \mathcal{E}(\gamma) \subset \mathcal{E}(\boldsymbol{x}),$$

and if γ is connected, so is $\boldsymbol{x}$.

We are going to compare the Mayer coefficient with a partition function for connected configurations,

$$Z_k^{\mathrm{cl}}(\beta) := \frac{1}{k!}\int_{(\mathbb{R}^d)^{k-1}} e^{-\beta U(0,x_2,\dots,x_k)} \mathbf{1}_{\text{conn}}(0,x_2,\dots,x_k)\mathrm{d}x_2\cdots\mathrm{d}x_k. \tag{24}$$

Lemma 4.1 (Cluster partition function vs. Mayer coefficient)**.**

$$\begin{aligned} &Z_k^{\mathrm{cl}}(\beta) - b_k(\beta) \\ &\qquad = \frac{1}{k!}\sum_{\gamma \text{ not conn.}} \int_{(\mathbb{R}^d)^{k-1}} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x})\mathbf{1}_{\mathrm{conn}}(\boldsymbol{x})\mathrm{d}x_2\cdots\mathrm{d}x_k,\ x_1 = 0 \end{aligned} \tag{25}$$

where the sum extends over graphs γ with vertices $\{1,\dots,k\}$ that are *not* connected.

Proof. In the integral for $Z_k^{\mathrm{cl}}(\beta)$, write as usual $\exp(-\beta v_{ij}) = 1 + f_{ij}$ and expand. This gives a sum over graphs. The graphs that are not connected correspond to the right-hand side of Eq. (25). The connected graphs yield an integral similar to Eq. (23), except that there is the additional characteristic function $\mathbf{1}_{\mathrm{conn}}(\boldsymbol{x})$. Noting that $\prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x})$ vanishes if γ is connected and $\boldsymbol{x}$ is not connected, we can drop the characteristic function without changing the value of the integral, and obtain Eq. (25). $\square$

For γ a graph with vertex set $\{1,\dots,k\}$, and $\boldsymbol{x} = (x_1,\dots,x_k) \in (\mathbb{R}^d)^k$ a configuration, write $\gamma^-(\boldsymbol{x}) \cap \gamma$ for the graph with vertices $1,\dots,k$ and edge set $\mathcal{E}(\gamma) \cap \mathcal{E}^-(\boldsymbol{x})$. Thus $\gamma^-(\boldsymbol{x}) \cap \gamma$ is the subgraph of γ consisting of the negative edges.

Lemma 4.2. Let $k \in \mathbb{N}$ and γ^- a graph with vertices $1,\dots,k$ with connected components of size $k_1,\dots,k_r$, $r \in \mathbb{N}$, $\sum_1^r k_i = k$. Then

$$\Bigg|\sum_{\gamma:\ \gamma^-(\boldsymbol{x})\cap\gamma = \gamma^-} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x})\Bigg| \le C_k \exp\big(-\beta(E_{k_1} + \cdots + E_{k_r})\big).$$

for some suitable $C_k > 0$ which does not depend on β or $r, k_1,\dots,k_r$. A similar estimate holds, for $r \ge 2$, if the sum is further restricted to graphs γ with $\gamma^-(\boldsymbol{x}) \cap \gamma = \gamma^-$ that are not connected.

Remark. The lemma is also true for a sum further restricted to graphs that are connected. It becomes wrong, in general, for doubly connected graphs.

Proof. Consider first the case $r = 1$, i.e., γ^- connected. Then

$$\sum_{\gamma:\, \gamma^-(\boldsymbol{x})\cap\gamma=\gamma^-} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}) = \Bigg(\prod_{(ij)\in\gamma^-} f_{ij}(\boldsymbol{x})\Bigg) \sum_{\mathcal{E}\subset\mathcal{E}^+(\boldsymbol{x})} \prod_{(ij)\in\mathcal{E}} f_{ij}(\boldsymbol{x})$$

$$= \Bigg(\prod_{(ij)\in\gamma^-} f_{ij}(\boldsymbol{x})\Bigg) \Bigg(\prod_{(ij)\in\mathcal{E}^+(\boldsymbol{x})} e^{-\beta v_{ij}(\boldsymbol{x})}\Bigg).$$

Noting that for a negative edge, $0 \leq f_{ij} \leq \exp(-\beta v_{ij})$, it follows that

$$0 \leq \sum_{\gamma:\, \gamma^-(\boldsymbol{x})\cap\gamma=\gamma^-} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}) \leq \exp\Big(-\beta\Big[\sum_{(ij)\in\gamma^+(\boldsymbol{x})} v_{ij}(\boldsymbol{x}) + \sum_{(ij)\in\gamma^-} v_{ij}(\boldsymbol{x})\Big]\Big)$$

$$\leq \exp\big(-\beta U(x_1,\dots,x_k)\big) \leq \exp(-\beta E_k).$$

Next, suppose that $r \geq 2$ and that we restrict the sum to graphs γ that have $\gamma^-(\boldsymbol{x}) \cap \gamma = \gamma^-$ and are disconnected. Such a graph can be constructed from γ^- in two steps: first, add positive intra-component edges, i.e., edges (ij) that have $v_{ij} \geq 0$ and connect two labels i, j belonging to the same connected component of γ^-. There is no restriction on the choices of such edges. Second, add positive inter-component edges. There is a restriction on how many edges we may add, since the resulting graph is required to be disconnected. Let $\mathcal{F}$ be the collection of allowed inter-component edge sets. The sum to be estimated takes the form

$$\sum_{\mathcal{E}\in\mathcal{F}} \Bigg(\prod_{(ij)\in\mathcal{E}} f_{ij}(\boldsymbol{x})\Bigg) \prod_{q=1}^{r} \Bigg[\Big(\prod_{(ij)\in\gamma_q^-} f_{ij}(\boldsymbol{x})\Big)\Big(\prod_{(ij)\in\gamma_q^+(\boldsymbol{x})} e^{-\beta v_{ij}(\boldsymbol{x})}\Big)\Bigg] \tag{26}$$

Here $\gamma_1^-, \dots, \gamma_r^-$ are the connected components of γ^-, and $\gamma_1^+(\boldsymbol{x}), \dots, \gamma_r^+(\boldsymbol{x})$ have as edge set the positive intra-component edges. Noting that $-1 \leq f_{ij} \leq 0$ for every positive edge, we deduce that (26) has absolute value bounded by

$$|\mathcal{F}|\, \exp\big(-\beta(E_{k_1} + \dots + E_{k_r})\big).$$

Since $|\mathcal{F}|$ can be bounded by some k-dependent constant, independent of γ^-, this concludes the proof. ☐

Proof of Theorem 3.1. Let $\boldsymbol{x} = (x_1, \dots, x_k)$ be an arbitrary configuration and γ a graph with vertices $1, \dots, k$ that is not connected. Then $\gamma^-(\boldsymbol{x}) \cap \gamma$ is not connected either. Therefore

$$\sum_{\gamma \text{ not conn.}} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}) = \sum_{\gamma^- \text{ not conn.}} \sum_{\substack{\gamma \text{ not conn.:} \\ \gamma^-(\boldsymbol{x})\cap\gamma=\gamma^-}} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}).$$

Lemma 4.2 then yields a bound on the absolute value of the form

$$C_k \exp\big(-\beta(E_{k_1} + \dots + E_{k_r})\big) \leq C_k \exp(-\beta(r-1)\varepsilon) \exp(-\beta E_k). \tag{27}$$

Here we have used that for potentials with an attractive tail, for suitable $\varepsilon > 0$ and all $k, q \in \mathbb{N}$, $E_{k+q} \leq E_k + E_q - \varepsilon$ (see the appendix in [9]). Since the set of connected configurations $(0, x_2, \ldots, x_k)$ has a finite Lebesgue volume, the integral on the right-hand side of Eq. (25) has an upper bound similar to the right-hand side of Eq. (27). On the other hand, because of the attractive tail of the potential, ground states are always connected. The continuity of the potential therefore yields

$$\lim_{\beta \to \infty} \beta^{-1} \log Z_k^{\mathrm{cl}}(\beta) = -E_k,$$

and we conclude from Lemma 4.1 that for every fixed k, as $\beta \to \infty$,

$$b_k(\beta) = (1 + O(e^{-\varepsilon\beta})) Z_k^{\mathrm{cl}}(\beta) = \exp\big(-\beta(E_k + o(1))\big). \qquad \square$$

5 Virial coefficients and absence of polyatomic gas

The virial coefficients have an expression similar to Eq. (23) for the Mayer coefficients. First we need a further graph theoretic notion. Let γ be a connected graph with vertices $1, \ldots, k$. A vertex j is called an *articulation point* if the graph $\gamma \backslash \{j\}$, obtained from γ by removing the vertex j and all incident edges, is not connected. A graph γ is called *doubly connected* if it has no articulation point. Let $\mathcal{G}_k^{\mathrm{dc}}$ be the doubly connected graphs with edges $1, \ldots, k$. It is known [7, Chapter 5] that

$$d_n(\beta) = \frac{1}{n!} \int_{(\mathbb{R}^d)^{n-1}} \sum_{\gamma \in \mathcal{G}_n^{\mathrm{dc}}} \prod_{(ij) \in \gamma} f_{ij}(\boldsymbol{x}) \mathrm{d}x_2 \cdots \mathrm{d}x_n, \quad x_1 = 0. \tag{28}$$

The d_n are, up to a factor and a shift in the index, often called “irreducible cluster integrals”; irreducibility refers to a product structure explained below.

Thus the Mayer coefficient $b_n(\beta)$ is the sum of $d_n(\beta)$ and a sum over graphs that are not doubly connected. We will not estimate $d_n(\beta)$ directly, but instead express $d_n(\beta)$ as a combination of $b_k(\beta)$'s and then apply Theorem 3.1.

For this purpose the following product structure, exploited in [14], proves useful: let γ be a connected graph with articulation point j. Call γ_1', γ_2' the connected graphs obtained from γ by removing the articulation point and all incident edges, and γ_1, γ_2 the graphs obtained by adding back to γ_1' (resp. γ_2') the articulation point j and incident edges. Then the integral corresponding to the graph γ in Eq. (28) (without the factorial) is a product of similar integrals corresponding to the graphs γ_1 and γ_2. The simplest example happens for $n = 3$ and the graph with articulation point 1, noting that

$$\int_{(\mathbb{R}^d)^2} f_{12}(\boldsymbol{x}) f_{13}(\boldsymbol{x}) \mathrm{d}x_2 \mathrm{d}x_3 = \Big(\int_{\mathbb{R}^d} f_{12}(0, x_2) \mathrm{d}x_2\Big)\Big(\int_{\mathbb{R}^d} f_{13}(0, x_3) \mathrm{d}x_3\Big).$$

This product structure can be iterated and, in the end, we can group graphs whose doubly connected components have the same supports $X_1, \ldots, X_r$, which necessarily satisfy

$$\bigcup_{i=1}^n X_i = \{1, \ldots, n\}, \quad 1 + \sum_{i=1}^n \big(|X_i| - 1\big) = 1.$$

Let $B_k(\beta) := k!b_k(\beta)$, $D_k(\beta) = k!d_k(\beta)$. We obtain

$$B_n(\beta) = \sum_{\{X_1,\ldots,X_r\}} D_{|X_1|}(\beta)\cdots D_{|X_r|}(\beta)$$

with a sum over all set collections possibly coming from the doubly connected components of a graph; $D_n(\beta)$ appears as the unique term for $r=1$. The relation can be inverted,

$$D_n(\beta) = \sum_{r\geq 1}(-1)^{r-1}\sum_{\{X_1,\ldots,X_r\}} B_{|X_1|}(\beta)\cdots B_{|X_r|}(\beta). \tag{29}$$

This is the expression we will work with. The formula becomes very natural, and can be rigorously proven, by a cluster expansion in the canonical ensemble, as was recently done in [14], see Appendix C. We rewrite Eq. (29) as follows:

Lemma 5.1. The virial coefficients are of the form

$$D_n(\beta) = B_n(\beta) + \sum_{r\geq 2}(-1)^{r-1}\sum_{k_1,\ldots,k_r}{}' a(k_1,\ldots,k_r)B_{k_1}(\beta)\cdots B_{k_r}(\beta) \tag{30}$$

with $\sum'$ the sum over all integers $k_1,\ldots,k_r \geq 2$ such that

$$1 + (k_1-1)+\cdots+(k_r-1) = n, \tag{31}$$

and $a(k_1,\ldots,k_r)\in\mathbb{N}>0$ are non-zero integers.

The lemma enables us to deduce the low-temperature asymptotics of virial coefficients from the asymptotics of Mayer coefficients as given in Theorem 3.1, provided we have some control over energy sums $E_{k_1}+\cdots+E_{k_r}$. Here condition (19) comes into play.

Lemma 5.2. Suppose Eq. (19) holds for all $m,n\in\mathbb{N}$. Then, for all $r,k_1,\ldots,k_r\geq 2$ satisfying Eq. (31),

$$E_n \leq E_{k_1}+\cdots+E_{k_r}. \tag{32}$$

If the inequality (19) is strict for all m,n, then the previous inequality is strict too.

Proof. We proceed by induction over r. For $r=2$, the inequality (32) is the same as (19), and true by assumption. For the induction step, suppose that the statement is true, at r, for all $n\in\mathbb{N}$. Let $k_1,\ldots,k_r$ satisfy Eq. (31). Then, by Eq. (19), for all $k_{r+1}\geq 2$,

$$E_{1+(n-1)+(k_{r+1}-1)} \leq E_n + E_{k_{r+1}} \leq (E_{k_1}+\cdots+E_{k_r}) + E_{k_{r+1}},$$

which proves the claim. The procedure for strict inequalities is exactly the same. □

Prop. 3.10 is an immediate consequence.

Proof of Prop. (3.10). By Lemma 5.2 and Theorem 3.1, all terms in the sum (30) are of order at most $\exp(-\beta E_n(1+o(1))$. If the inequality (19) is strict, the dominant contribution comes from $B_n(\beta)$ ($r=1$), which is equal to $\exp(-\beta E_n(1+o(1)))$, again by Theorem 3.1. □

Lemma 5.3. Suppose that $\mu_1 = E_2 < e_\infty$ and $E_k/(k-1) > E_2$ for all $k \geq 3$. Then, for all $k_1, \ldots, k_r \geq 2$ and $r \geq 2$ satisfying Eq. (31),

$$(n-1)E_2 \leq E_{k_1} + \cdots + E_{k_r}.$$

with equality if and only if $r = n-1$ and $k_1 = k_2 = \cdots = k_r = 2$.

Thus the main contribution to $b_n(\beta) - d_n(\beta)$ comes from graphs whose doubly connected components all have size 2.

Proof. By assumption, $E_k > (k-1)E_2$ for all $k \geq 3$, from which we obtain

$$E_{k_1} + \cdots + E_{k_r} \geq \sum_1^r (k_i - 1)E_2 = (n-1)E_2$$

with equality if and only if all k_i's are equal to 2. □

Proof of Prop. 3.11. By Lemma 5.3 and Theorem 3.1, in Eq. (30) all terms are negligible except the one for $r = n-1$, $k_1 = \cdots = k_r = 2$. □

We conclude with the proof of the sufficient criteria for the absence of polyatomic gas.

Proof of Prop. 3.7. 1. An induction on n shows that if Eq. (19) holds, then for all $n \in \mathbb{N}$ and $p \in \mathbb{N}$

$$\frac{E_{2^n(p-1)+1}}{2^n(p-1)} \leq \frac{E_p}{p-1}. \tag{33}$$

Letting $n \to \infty$, we obtain $e_\infty \leq E_p/(p-1)$ for all p, whence $\mu_1 \geq e_\infty$. Since in any case $\mu_1 \leq e_\infty$, we get $\mu_1 = e_\infty$.

2. Suppose $v(r) \leq 0$ for all $r > r_{\text{hc}}$. Let $m, n \in \mathbb{N}$ and $\boldsymbol{x}$, $\boldsymbol{y}$ be $m+1$ and $n+1$-particle ground states. We can construct an $m+n+1$-configuration $\boldsymbol{z}$ by shifting and rotating $\boldsymbol{x}$ and $\boldsymbol{y}$, and then gluing them in one point, in such a way that all points except the two points that got glued have distance $> r_{\text{hc}}$, (if $v(r_{\text{hc}}) \leq 0$) or $> r_{\text{hc}}$ (if $v(r_{\text{hc}}) = \infty$).

The energy of the resulting configuration is $E_{m+1} + E_{n+1} +$ the interaction between the two cloud of m and n particles, excluding the glued particle. By construction, the interaction is finite and, therefore, negative. It follows that $E_{m+n+1} \leq U(\boldsymbol{z}) \leq E_{m+1} + E_{n+1}$. Since m and n were arbitrary, applying the sufficient criterion from 1., we get $\mu_1 = e_\infty$. □

6 Bounds for the density $\rho(\beta, \mu)$

In this section we prove Theorems 3.2 and 3.6.

Proof of Theorem 3.2. 1. Suppose $\mu > e_\infty + C\beta^{-1}\log\beta$ with $C > C_0$. Write $\rho = \exp(-\beta\nu)$ and $\mu(\nu) = \inf_{k\in\mathbb{N}}(E_k - \nu)/k$. For $\nu \leq \nu^*$, $\mu(\nu) = e_\infty$, and for $\nu > \nu^*$, $\mu(\nu) < e_\infty$, see Appendix A. Using Eq. (14),

$$\begin{aligned} p(\beta,\mu) &= \sup_{0<\rho<\rho_{\mathrm{cp}}} (\mu\rho - f(\beta,\rho)) \\ &\geq \sup_{0<\rho<\rho_0} (\mu\rho - f(\beta,\rho)) \\ &\geq \sup_{0<\rho<\rho_0} \Big(\mu\rho - \mu(\nu)\rho - C_0\rho\beta^{-1}\log\beta\Big) \\ &\geq \sup_{0<\rho<\rho_0} \Big((\mu - e_\infty - C_0\beta^{-1}\log\beta)\rho\Big) \\ &= \rho_0\big(\mu - e_\infty - C_0\beta^{-1}\log\beta\big), \end{aligned}$$

since $\mu > e_\infty + C_0\beta^{-1}\log\beta$. On the other hand, let $\rho = \rho(\beta,\mu)$ be any maximizer of $\rho\mu - f(\beta,\rho)$. If $\rho \geq \rho_0$, we are done. If $\exp(-\beta\nu^*) \leq \rho \leq \rho_0$, then

$$\rho(\mu - e_\infty + C_0\beta^{-1}\log\beta) \geq p(\beta,\mu) \geq \rho_0\big(\mu - e_\infty - C_0\beta^{-1}\log\beta\big),$$

which gives

$$\mu \leq e_\infty + C_0\frac{\rho_0+\rho}{\rho_0-\rho}\beta^{-1}\log\beta.$$

Since $\mu \geq e_\infty + C\beta^{-1}\log\beta$, we obtain $C_0(\rho_0+\rho) \geq C(\rho_0-\rho)$ whence

$$\rho \geq \frac{C-C_0}{C+C_0}\,\rho_0.$$

Thus we are left with the case $\rho < \exp(-\beta\nu^*)$, i.e., $\nu > \nu^*$. Noting $\mu(\nu) \geq e_\infty - \nu$ for all ν, we get

$$\rho\mu - \rho(e_\infty - \nu) + C_0\rho\beta^{-1}\log\beta \geq p(\beta,\mu) \geq \rho_0\big(\mu - e_\infty - C_0\beta^{-1}\log\beta\big).$$

Since $\rho\nu = \nu e^{-\beta\nu} \leq \beta^{-1}$, we obtain

$$\begin{aligned} \mu &\leq e_\infty + \frac{\beta^{-1} + C_0(\rho_0+\rho)\beta^{-1}\log\beta}{\rho_0-\rho} \\ &\leq e_\infty + \frac{\beta^{-1} + C_0(\rho_0+e^{-\beta\nu^*})\beta^{-1}\log\beta}{\rho_0 - e^{-\beta\nu^*}} = e_\infty + C_0(1+o(1))\beta^{-1}\log\beta, \end{aligned}$$

which for sufficiently large β is in contradiction with the assumption on μ.

2. For $\mu < e_\infty - C\beta^{-1}\log\beta$ with $C > 1$ we use Theorem 3.1. Define $R > 0$ by

$$Re^{-\beta e_\infty}\beta||\bar{v}||_1 = 1/e, \quad ||\bar{v}||_1 = B(0,r_{\mathrm{hc}}) + \int_{|x|>r_{\mathrm{hc}}} |v(|x|)|\mathrm{d}x \tag{34}$$

see Eq. (9). For $K \in \mathbb{N}$, using Eq. (10), we have

$$\begin{aligned}\rho(\beta,\mu) &\le \sum_{k=1}^{K} k\exp\bigl(\beta(k\mu - E_k + o(1))\bigr) + \Bigl(\frac{z}{R}\Bigr)^K z \sum_{k=K+1}^{\infty} k b_k(\beta) R^{k-1}\\ &\le e^{-\beta(\nu^*+o(1))} + \Bigl(\frac{z}{R}\Bigr)^K (e-1) z e^{-\beta e_\infty}\\ &= e^{-\beta(\nu^*+o(1))}\\ &\qquad + (e-1)\exp\Bigl(K\Bigl[(-C+1)\beta^{-1}\log\beta + \beta^{-1}(1-\log\|\bar{v}\|_1)\Bigr]\Bigr)\end{aligned}$$

As $\beta \to \infty$, the second term is of order $\beta^{-K(C-1+o(1))}$. Since K could be chosen arbitrarily large, this completes the proof of Theorem 3.2. ☐

Proof of Theorem 3.6. We proceed analogously to the proof of the second part of Theorem 3.2. Let $R = \exp(\beta(e_\infty + o(1)))$ be as in Eq. (34). Fix $\mu < e_\infty$. For $K \in \mathbb{N}$, using Eq. (10),

$$\Bigl|\rho(\beta,\mu) - \sum_{k=1}^{K} k\exp\bigl(\beta(k\mu - E_k + o(1))\bigr)\Bigr| \le \Bigl(\frac{z}{R}\Bigr)^K (e-1) z e^{-\beta e_\infty}. \tag{35}$$

Since $E_k - k\mu = k(e_\infty - \mu + o(1)) \to \infty$ as $k \to \infty$, there is a finite $k(\mu)$ minimizing $E_k - k\mu$. Choosing K large enough so that $K \ge k(\mu)$ and $K(e_\infty - \mu) > |\inf_k(E_k - k\mu)|$, Eq. (17) follows from the inequality (35).

If $(E_k - k\mu)_{k\in\mathbb{N}}$ has a unique minimizer $k(\mu) \in \mathbb{N}$, the previous argument actually yields

$$\rho(\beta,\mu) = k(\mu) b_{k(\mu)}(\beta) e^{\beta k(\mu)\mu}(1+o(1)).$$

An analogous argument gives

$$\beta p(\beta,\mu) = b_{k(\mu)}(\beta) e^{\beta k(\mu)\mu}(1+o(1)),$$

and Eq. (17) follows. ☐

7 Asymptotics of R^{May}, ρ_{sat}, ρ^{May} and R^{vir}

Here we prove Theorems 3.5 and 3.8.

Proof of Theorem 3.5. If the activity satisfies Eq. (9), then $z < R_\Lambda^{\mathsf{May}}(\beta)$, see [13, Theorem 2.1], and the lower bounds follow just as in Eq. (11). For the upper bound, we use a result from [12]: for all $k \in \mathbb{N}$,

$$R_\Lambda^{\mathsf{May}}(\beta) \le \Bigl(\frac{k\exp(-\beta e_\infty)}{(k-1)|b_{k,\Lambda}(\beta)|}\Bigr)^{1/(k-1)}.$$

Here $b_{k,\Lambda}(\beta)$ are the coefficients of the finite volume pressure-density series. They converge to $b_k(\beta)$ as $|\Lambda| \to \infty$, whence

$$\limsup_{|\Lambda|\to\infty} R_\Lambda^{\mathsf{May}}(\beta) \leq \Big(\frac{k\exp(-\beta e_\infty)}{(k-1)|b_k(\beta)|}\Big)^{1/(k-1)}.$$

We deduce from Theorem 3.1 that for every $k \in \mathbb{N}$,

$$\limsup_{\beta\to\infty} \limsup_{|\Lambda|\to\infty} \log R_\Lambda^{\mathsf{May}}(\beta) \leq \frac{-e_\infty + E_k}{k-1}.$$

We conclude by letting $k \to \infty$ in the upper bound. □

For the proof of Theorem 3.8, we start with the lower bound on the density of saturated gas $\rho_{\mathrm{sat}}(\beta)$ and the density $\rho^{\mathsf{May}}(\beta)$ delimiting the physical parameter region covered by the Mayer series.

Proof of Eq. (20). We observe that $\rho_{\mathrm{sat}}(\beta) \geq \rho^{\mathsf{May}}(\beta) \geq \rho(\beta,\mu)$ for all β and all $\mu \leq \mu_{\mathrm{sat}}(\beta)$. By Eq. (11) and Theorem 3.6, it follows that for every $\mu < e_\infty$,

$$\liminf_{\beta\to\infty} \beta^{-1} \log \rho_{\mathrm{sat}}(\beta) \geq \liminf_{\beta\to\infty} \beta^{-1} \log \rho^{\mathsf{May}}(\beta) \geq \sup_{k\in\mathbb{N}} (k\mu - E_k).$$

Noting that

$$\sup_{\mu<e_\infty} \sup_{k\in\mathbb{N}} (k\mu - E_k) = \sup_{k\in\mathbb{N}} \sup_{\mu<e_\infty} (k\mu - E_k) = \sup_{k\in\mathbb{N}} (ke_\infty - E_k) = -\nu^*,$$

we deduce Eq. (20). □

Proof of Eq. (21). Write the pressure-density series as $\beta p = \rho + \sum_{n\geq 2} c_n(\beta)\rho^n$. We start from the contour integral, see [10] or [16, Chapter 4.3],

$$c_n(\beta) = \frac{\beta^{-1}}{2\pi i} \oint_C \frac{\mathrm{d}z}{nz\rho(z)^{n-1}}.$$

Here the density $\rho(z) = \sum_{n=1}^\infty n b_n(\beta) z^n$ is extended to complex activities z, and we integrate on a circle C of radius $\exp(\beta\mu) < \exp(\beta\mu_1)$. For β sufficiently large, we know that $\exp(\beta\mu) < R^{\mathsf{May}}(\beta)$, and we are going to check that $|\rho(z)| > 0$ for $|z| = \exp(\beta\mu)$. To this aim we write

$$|\rho(z)| \geq |z| \Big(1 - \sum_{k\geq 2} k b_k(\beta) |z|^{k-1}\Big).$$

For every fixed $K \geq 2$, as $\beta \to \infty$,

$$\begin{aligned}
\sum_{k=2}^K k b_k(\beta) (e^{\beta\mu})^{k-1} &= \sum_{k=2}^K k \exp\Big(\beta(k-1)\big[\mu - \frac{E_k}{k-1} + o(1)\big]\Big) \\
&\leq \sum_{k=2}^K k \exp\Big(\beta(k-1)\big(\mu - \mu_1 + o(1)\big)\Big) \\
&\leq \mathrm{const}(K,\mu) \exp\Big(\beta\big(\mu - \mu_1 + o(1)\big)\Big).
\end{aligned}$$

Furthermore, if $R = \exp(\beta(e_\infty + o(1)))$ is as in Eq. (34), and β sufficiently large so that $\exp(\beta\mu)/R \leq \exp(-\beta\varepsilon)$ with suitable $\varepsilon > 0$,

$$\sum_{k=K+1}^{\infty} k b_k(\beta)|z|^{k-1} \leq \Big(\frac{z}{R}\Big)^K (e-1)\exp(-\beta e_\infty)$$
$$\leq (e-1)\exp\big(-\beta(K\varepsilon + e_\infty)\big).$$

We choose $K \in \mathbb{N}$ such that $K\varepsilon + e_\infty > \mu_1 - \mu$ and combine the previous estimates. We obtain that as $\beta \to \infty$, $\sum_{k\geq 2} k b_k(\beta)|z|^{k-1}$ is of order at most $\exp(\beta(\mu - \mu_1))$ and, in particular, goes to 0, so that $\rho(z) \neq 0$.

We can plug the lower bound for $|\rho(z)|$ into the contour integral. This yields

$$|c_n| \leq \frac{\beta^{-1}}{n} \times \frac{1}{\big[(1+o(1))\exp(\beta\mu)\big]^{n-1}}$$

whence $R^{\mathsf{vir}}(\beta) \geq (1+o(1))\exp(\beta\mu)$ and

$$\liminf_{\beta\to\infty} \beta^{-1} \log R^{\mathsf{vir}}(\beta) \geq \mu.$$

This is true for every $\mu < \mu_1 = -\nu_1$, and the inequality (21) follows. ☐

Proposition 7.1. *Under the assumptions of Theorem 3.8, suppose that in addition $\mu_1 = E_2 < e_\infty$. Then, for suitable $\beta_1, C_1, \varepsilon > 0$ and all $\beta \geq \beta_1$, the equation*

$$\frac{\mathrm{d}\rho}{\mathrm{d}z}(z) = 1 + \sum_{k=2}^{\infty} k^2 b_k(\beta) z^{k-1} = 0$$

has a solution $z_0(\beta)$ at distance $\leq C_1 \exp(-\varepsilon\beta)/b_2(\beta)$ of $-1/(4b_2(\beta))$, and $\rho(z_0(\beta)) \neq 0$. If $\mu_1 = E_p/(p-1) < e_\infty$ for some $p \geq 3$, a similar statement holds with $-1/4b_2(\beta)$ replaced with one of the roots of the equation $1 + p^2 b_p(\beta) z^p = 0$.

Proof of Eq. (21). For sufficiently small ρ, the density-activity relation can be inverted: there is function $g(\rho)$, analytic in a domain containing 0, such that for small z, $g(\rho(z)) = z$, and the restriction of g to some neighborhood of 0 is actually injective. The virial series is given by the composition

$$G(\rho) = \sum_{n=1}^{\infty} c_n \rho^n = \sum_{n=1}^{\infty} b_n \Big(g(\rho)\Big)^n = F(g(\rho)).$$

For sufficiently small z, we have $g(\rho(z)) = z$ and

$$G'(\rho(z)) = \frac{\rho(z)}{z\rho'(z)}. \tag{36}$$

The relation extends by analyticity to every domain D such that ρ is analytic in $z \in D$ and G is analytic in $\rho(D)$. Now, from Prop. 7.1, we know that $\rho'(z_0)/\rho(z_0) = 0$ with $|z_0| < R^{\mathsf{May}}$.

Eq. (36) cannot be true at $z = z_0$. Let D be an open disk centered at 0 with radius $> |z_0|$. The function G cannot be analytic in all of $\rho(D)$, hence there must be some $z \in D$ such that

$$R^{\mathsf{vir}} \leq |\rho(z)| \leq \sum_{k=1}^{\infty} k|b_k(\beta) z^k|. \tag{37}$$

Let $\delta > 0$ small enough so that $\mu_1 + \delta < e_\infty$. For sufficiently large β, we may choose $|z| \leq \exp(\beta(\mu_1 + \delta))$ in Eq. (37). The usual procedure shows that

$$\limsup_{\beta \to \infty} \beta^{-1} \log R^{\mathsf{vir}}(\beta) \leq \sup_{k \in \mathbb{N}} \bigl(k(\mu_1 + \delta) - E_k\bigr).$$

Noting that $\sup_k (k\mu - E_k)$ is locally bounded and convex, hence continuous, in $\mu < e_\infty$, we can let $\delta \searrow 0$, which yields

$$\limsup_{\beta \to \infty} \beta^{-1} \log R^{\mathsf{vir}}(\beta) \leq \sup_{k \in \mathbb{N}} (k\mu_1 - E_k) = -\nu_1. \qquad \square$$

Proof of Prop. 7.1. The idea is to use an implicit function theorem, perturbing around $\exp(-\beta) = 0$. We give the proof for $\mu_1 = E_2 < \infty$. The proof for $\mu_1 = E_p/(p-1)$, $p \geq 3$, is similar. For sufficiently large β, $b_2(\beta) > 0$. Let

$$a_k(\beta) := k^2 \frac{b_k(\beta)}{b_2(\beta)^{k-1}}, \quad \hat{z} := b_2(\beta) z.$$

The equation to be solved becomes

$$1 + 4\hat{z} + \sum_{k \geq 3} a_k(\beta) \hat{z}^{k-1} \stackrel{!}{=} 0.$$

By assumption, for suitable $\Delta > 0$ and all $k \geq 3$, $E_k \geq \mu_1 + (k-1)\Delta$, and $\mu_1 = E_2 < e_\infty$. Therefore, for every fixed $k \geq 3$, as $\beta \to \infty$,

$$|a_k(\beta)| \leq k^2 \exp\bigl(-\beta(k-1)(\Delta + o(1))\bigr) \to 0.$$

Moreover, for every $s > 0$ and $K \in \mathbb{N}$,

$$\sum_{k=K+1}^{\infty} k^{1+s} \left| \frac{b_k(\beta)}{b_2(\beta)^{k-1}} \right| \leq \Bigl(\sup_{k \geq K} (k+1)^s (b_2(\beta) R)^{-k} \Bigr) (e-1) e^{-\beta e_\infty}.$$

with $R = \exp(\beta(e_\infty + o(1)))$ as in Eq. (34). Thus

$$b_2(\beta) R = \exp\bigl(\beta(e_\infty - E_2 + o(1))\bigr) \to \infty.$$

It follows that for every $s > 0$, and suitable $\varepsilon_s > 0$, as $\beta \to \infty$,

$$\sum_{k=3}^{\infty} k^s |a_k(\beta)| = O\bigl(\exp(-\varepsilon_s \beta)\bigr).$$

Now let X be the Banach space of sequences $(a_k)_{k\geq 3}$ with weighted norm $||\boldsymbol{a}|| := \sum_k k^s |a_k|$. Set

$$F(\boldsymbol{a}, \hat{z}) := 1 + 4\hat{z} + \sum_{k\geq 3} a_k \hat{z}^{k-1}.$$

The equation $F(\mathbf{0}, \hat{z}) = 0$ has the unique solution $\hat{z}_0 = -1/4$, and in a neighborhood of $(\mathbf{0}, \hat{z}_0)$, for suitable choice of s, F is continuously Fréchet-differentiable. Moreover $\partial_{\hat{z}} F(\mathbf{0}, \hat{z}) = 4 \neq 0$. As a consequence, we can apply a Banach space implicit function theorem. It follows in particular that as $||\boldsymbol{a}|| \to 0$, the equation $F(\boldsymbol{a}, \hat{z}) = 0$ has a solution $\hat{z}(\boldsymbol{a}) = \hat{z}_0 + O(||\boldsymbol{a}||)$. Applying this to $\boldsymbol{a}(\beta) = (a_k(\beta))_{k\in\mathbb{N}}$, we obtain the solution $b_2(\beta) z_0(\beta) = -1/4 + O(e^{-\beta\varepsilon_s})$.

For the density, we observe that

$$\rho(z_0(\beta)) = z_0(\beta)\Big(1 + 2b_2(\beta) z_0(\beta) + O(e^{-\varepsilon_s \beta})\Big) = -\frac{1}{2} z_0(\beta)(1 + O(e^{-\varepsilon_s\beta})).$$

It follows that for sufficiently large β, $\rho(z_0(\beta)) \neq 0$. ☐

A Two auxiliary variational problems

Throughout this section we assume that v is a stable pair potential with attractive tail. Consider the following two variational problems

$$\begin{aligned} \nu(\mu) &:= \inf_{k\in\mathbb{N}} (E_k - k\mu), \quad \mu \leq e_\infty, \\ \mu(\nu) &:= \inf_{k\in\mathbb{N}} \frac{E_k - \nu}{k}, \qquad \nu > 0. \end{aligned}$$

The first variational problem appears in Theorem 3.6, and minimizers $k(\mu)$ correspond to the favored size of molecules in the gas phase as $\beta \to \infty$ at fixed μ. The second problem appears in Eq. (14) and, as shown in [9], minimizers $k(\nu)$ correspond to favored cluster or molecule sizes as $\beta \to \infty$ and $\rho \to 0$ along $\rho = \exp(-\beta\nu)$, at fixed ν.

Recall that for potentials with an attractive tail, $\nu^* := \inf_k (E_k - k e_\infty) > 0$.

Lemma A.1 (Convexity, monotonicity and equivalence)**.** Let v be a stable pair interaction with attractive tail. Then:

1 The function $\mu \mapsto \nu(\mu)$ is strictly decreasing, piecewise affine and concave in $\mu \in (-\infty, e_\infty]$. The function $\nu \mapsto \mu(\nu)$ is decreasing, piecewise affine and concave in $\nu \in [0, \infty)$; it is strictly decreasing in $\nu \in [\nu^*, \infty)$ and equals $\mu(\nu) = e_\infty$ for $\nu \leq \nu^*$.

2 The function $\nu(\mu)$ is the inverse of $[\nu^*, \infty) \ni \nu \mapsto \mu(\nu)$: for $\mu \leq e_\infty$ and $\nu \geq \nu^*$,

$$\nu = \nu(\mu) \Leftrightarrow \mu = \mu(\nu).$$

The reciprocity of $\mu(\nu)$ and $\nu(\mu)$ is analogous to the equivalence of the grand-canonical and the constant pressure ensembles. Indeed, the pressure and the Gibbs energy (per particle) are both obtained as Legendre transforms of the free energy, one with respect to the density, the other with respect to the volume per particle,

$$p(\beta,\mu) = \sup_\rho \big(\mu\rho - f(\beta,\rho)\big), \quad g(\beta,p) = \inf_v \big(\tilde f(\beta,v) + pv\big),$$

with $\tilde f(\beta,v) = v f(\beta,v^{-1})$ the free energy per particle. Equivalence of ensembles here means that $p(\beta,\cdot)$ and $g(\beta,\cdot)$ are reciprocal: the Gibbs energy is the same as the chemical potential.

Similarly, $\mu(\nu)$ looks like a Legendre transform of $k \mapsto E_k$ with respect to k, while $\nu(\mu)$ looks like a Legendre transform of E_k/k with respect to $1/k$, which should be compared with the relations $v = 1/\rho$, $\tilde f(\beta,v) = f(\beta,\rho)/\rho$.

Proof of Lemma A.1. 1. The statement for the function $\mu(\nu)$ was proven in [4, 9]. For $\nu(\mu)$, we note that it is the infimum of a family of decreasing, affine functions and therefore concave and decreasing. Moreover it is almost everywhere differentiable, with derivative $-k(\mu)$, the minimizer of $E_k - k\mu$. In particular $k(\mu) \geq 1$, hence $\nu(\mu)$ is strictly decreasing.

2. We prove "$\Rightarrow$". The proof of the converse is similar. Thus let $\mu \leq e_\infty$ and $\nu = \inf_k(E_k - k\mu)$. Clearly, $\nu \leq \inf_k(E_k - ke_\infty) = \nu^*$, and for every $k \in \mathbb{N}$,

$$\nu \leq E_k - k\mu \ \Rightarrow \mu \leq \frac{E_k - \nu}{k},$$

whence $\mu \leq \mu(\nu)$. On the other hand, if $\mu < e_\infty$, then $E_k - k\mu \geq \nu^* + k(e_\infty - \mu) \to \infty$ as $k \to \infty$, so there must be a finite k such that $\nu = E_k - k\mu$. It follows that $\mu = (E_k - \nu)/k \geq \mu(\nu)$, whence $\mu = \mu(\nu)$. If $\mu = e_\infty$, then $\nu = \nu^*$ and the claim follows from the general inequality $\mu(\nu) \leq e_\infty$. □

Lemma A.2 (Comparison of thresholds)**.** Let

$$\mu_1 := \inf_{k\geq 2} \frac{E_k}{k-1}, \quad \nu_1 = -\mu_1.$$

Then

- either $\mu_1 = e_\infty$ and $\nu^* = -e_\infty = \nu_1$,
- or $\mu_1 < e_\infty$ and $\nu^* < -e_\infty < \nu_1$.

Proof. Lemma A.1 implies the general bounds $\mu_1 \leq e_\infty$ and $\nu_1 \geq \nu^*$. Moreover, by definition, $\nu^* \leq E_1 - e_\infty = -e_\infty$ and

$$\nu_1 = \sup_k \frac{E_k}{1-k} \geq \lim_{k\to\infty} \frac{E_k}{1-k} = -e_\infty$$

so that $\nu^* \leq -e_\infty \leq \nu_1$. If in addition $\mu_1 = e_\infty$, then $\nu_1 = -e_\infty$ and for all $k \in \mathbb{N}$, $E_k \geq (k-1)e_\infty$ from which we get $\nu^* = \inf_k(E_k - ke_\infty) \geq -e_\infty$. Since in any case $\nu^* \leq e_\infty$, we get $\nu^* = e_\infty$.

If $\mu_1 < e_\infty$, then $\nu_1 > e_\infty$ and there is a $p \in \mathbb{N}$ such that $\mu_1 = E_p/(p-1) < e_\infty$. It follows that

$$\nu^* \leq E_p - pe_\infty = (p-1)(\mu_1 - e_\infty) - e_\infty < -e_\infty. \qquad \square$$

Lemma A.3 ("Phase" diagram). 1 For $\mu < \mu_1$, $E_k - k\mu$ has the unique minimizer $k(\mu) = 1$. Similarly, for $\nu > \nu_1$, $(E_k - \nu)/k$ has the unique minimizer $k(\nu) = 1$.

2 For $\mu_1 < \mu < e_\infty$, every minimizer is finite and larger or equal to 2; similarly for $\nu^* < \nu < \nu_1$.

3 For $\nu < \nu^*$, $(E_k - \nu)/k$ has no finite minimizer.

Proof. The statements for the $(E_k - \nu)/k$, except the formula for ν_1, were proven in [4, 9]. The statements for $E_k - k\mu$ follow with the help of the reciprocity from Lemma A.1.

It remains to check the nature of the transition at μ_1 if $\mu_1 < e_\infty$. To this aim we note that $\nu(\mu) = -\mu$ if and only if $E_k - k\mu \geq -\mu$ for all $k \geq 2$, i.e., if and only if $E_k/(k-1) \geq \mu$ for all $k \geq 2$, which is precisely the condition $\mu_1 \geq \mu$. □

B Free energy at low temperature and low density

Here we give a sketch of the proof of (14). The primary aim is to show that ρ_0 can be chosen indeed of the order of the preferred ground state density, $\rho_0 \approx 1/a^d$. For the sake of completeness, we also make a remark on how Eq. (14) should be modified for potentials without attractive tail.

Potentials with attractive tail Let $Z_k^{\mathrm{cl}}(\beta)$ be the cluster partition function from (24) above. Then [9, Lemma 3.1]

$$Z_\Lambda(\beta, N) \leq \sum_{\sum k N_k = N} \frac{(|\Lambda| Z_k^{\mathrm{cl}}(\beta))^{N_k}}{N_k!}$$

The sum is over integers $N_1, \dots, N_N \in \mathbb{N}_0$ such that $\sum_k k N_k = N$. The integers describe a partition of the N particles into clusters, i.e., groups of particles close in space. Using that for suitable $c > 0$ and all $\beta > 0$ and $k \in \mathbb{N}$,

$$Z_k^{\mathrm{cl}}(\beta) \leq \exp(-\beta E_k) \exp(ck),$$

[9, Lemma 4.3] we deduce that $-\beta f(\beta, \rho)$ is upper bounded by the supremum of

$$c\rho - \beta\Big(\sum_{k\in\mathbb{N}} \rho_k E_k + (\rho - \sum_{k\in\mathbb{N}} \rho_k) e_\infty\Big) + \sum_{k\in\mathbb{N}} \rho_k (1 - \log \rho_k).$$

over all $(\rho_k)_{k\in\mathbb{N}} \in [0,\infty)^{\mathbb{N}}$ such that $\sum_1^\infty k\rho_k \leq \rho$ (think $\rho_k = N_k/|\Lambda|$). Next, we observe that the mixing entropy can be bounded as $\sum_k \rho_k \log(\rho_k/\rho) \geq -2\rho$, for all $\rho > 0$ and all admissible (ρ_k), see [9, Lemma 4.2]. Therefore we obtain

$$\begin{aligned} -\beta f(\beta,\rho) &\leq (c+3)\rho \\ &\quad - \beta \inf\Big\{ (\rho - \sum_{k\in\mathbb{N}} k\rho_k) e_\infty + \sum_{k\in\mathbb{N}} \rho_k (E_k + \beta^{-1}\log\rho) \,\Big|\, \sum_k k\rho_k \leq \rho \Big\}, \end{aligned}$$

whence

$$f(\beta,\rho) \geq -(c+3)\beta^{-1}\rho + \rho \inf_{k\in\mathbb{N}} \frac{E_k + \beta^{-1}\log\rho}{k}, \tag{38}$$

for all $\beta > 0$ and all $\rho > 0$.

It remains to obtain an upper bound for the free energy, or a lower bound for the partition function. Consider first the case $\nu^* > 0$ and $\rho \geq \exp(-\beta\nu^*)$. In this case the auxiliary variational problem has e_∞ as its minimizer. We lower bound the partition function by integrating only over a small neighborhood of the N-particle ground state, and deduce $-\beta f(\beta,\rho) \geq e_\infty - C\beta^{-1}\log\beta$ for suitable C and sufficiently large β. Note that this is possible if ρ is smaller than the density of the ground state, $\rho < 1/a^d$.

Next, consider the case $\rho = \exp(-\beta\nu) < \exp(-\beta\nu^*)$. In this case $(E_k - \nu)/k$ has a finite minimizer $k = k(\nu) \in \mathbb{N}$. We lower bound the partition function for a cube $\Lambda = [0,L]^d$ and $N \in k\mathbb{N}$ particles as follows: we split the cube into M small cubes ("cells") with side length of the order $ak^{1/d}$ and mutual distance R. Here R is of the order of the potential range, and $ak^{1/d}$ is large enough so that a k-particle ground state fits into the small cube, as in Assumption 2. We can place approximately $M = |\Lambda|/(ak^{1/d} + R)^d$ small cubes in that way. We consider configurations in which particles form clusters of size k close to their ground state, such that each cluster fits completely into a small cube, and there is at most one cluster per cell.

We refer the reader to [9] for the details and content ourselves with the following remark: the procedure works provided the the number M of available cells is larger than N/k. This gives the condition

$$\rho < (a + Rk^{-1/d})^{-d}.$$

Hence if we choose β large enough so that $\exp(-\beta\nu^*) \leq (a+R)^{-d}$, the condition is certainly fulfilled for every $\rho \leq \exp(-\beta\nu^*)$.

Remember that for $\rho \geq \exp(-\beta\nu^*)$, we are in the first case considered above and we only need $\rho \leq 1/a^d \approx$ ground state density. Therefore, in the end, all we need is the condition $\rho < \rho_0$ with ρ_0 of the order of $1/a^d$.

Potentials without attractive tail If v has no attractive tail, we might have $\nu^* = 0$, and ground states are not necessarily connected. Set $E_1^{\mathrm{cl}} = E_1 = 0$ and

$$E_k^{\mathrm{cl}} := \inf\bigl\{U(x_1,\dots,x_k) \mid (x_1,\dots,x_k) \in (\mathbb{R}^d)^k\ R\text{-connected}\bigr\} \geq E_k.$$

The lower bound (38) is still true, but can be improved by replacing E_k by E_k^{cl}. In fact, indices k with $E_k^{\mathrm{cl}} > E_k$ can be dropped altogether: if $E_k^{\mathrm{cl}} > E_k$, then for suitable $r \geq 2$, $k_1 + \cdots + k_r = k$,

$$E_k^{\mathrm{cl}} > E_k = E_{k_1}^{\mathrm{cl}} + \cdots + E_{k_r}^{\mathrm{cl}} \tag{39}$$

Suppose that for some $\nu > 0$, $(E_{k_i}^{\mathrm{cl}} - \nu)/k_i \geq (E_k^{\mathrm{cl}} - \nu)/k$ for all k. Then

$$\sum_1^r E_{k_i}^{\mathrm{cl}} \geq \sum_1^r \bigl(\nu + k_i \frac{E_k^{\mathrm{cl}} - \nu}{k}\bigr) = (r-1)\nu + E_k^{\mathrm{cl}} > E_k^{\mathrm{cl}},$$

contradicting (39). Thus

$$\inf_{k\in\mathbb{N}} \frac{E_k^{\mathrm{cl}} - \nu}{k} = \inf\Big\{ \frac{E_k - \nu}{k} \mid k \in \mathbb{N},\ E_k = E_k^{\mathrm{cl}} \Big\}$$

is the appropriate auxiliary variational problem to be substituted into Eq. (14). The density ρ_0 can be chosen of the order of $(a+R)^{-1/d}$.

Non-negative potentials When $v \geq 0$, the situation becomes particularly simple: we have $\nu^* = 0$ and for all $\nu > 0$,

$$\inf_{k\in\mathbb{N}} \frac{E_k - \nu}{k} = \inf_{k\in\mathbb{N}} \frac{E_k^{\mathrm{cl}} - \nu}{k} = -\nu$$

and $k(\nu) = 1$ is the unique minimizer. Eq. (14) is replaced by the following: For sufficiently low temperature and density ρ smaller than or of the order of $1/R^d$,

$$\big| f(\beta,\rho) - \beta^{-1} \rho \log \rho \big| \leq C \rho \beta^{-1} \log \beta$$

and we recognize the free energy $\beta^{-1}\rho(\log\rho - 1)$ of an ideal gas.

C Cluster expansion in the canonical ensemble

Eq. (29) for the coefficients for the free energy-density series can be derived directly, without any need to refer to doubly connected graphs as in Eq. (28). This was recently shown in [14] with the help of a cluster expansion in the canonical ensemble. The aim of this section is to give some key ideas, without any proofs – for those we refer the reader to [14].

The starting point is an expression of the canonical partition function as a sum over set partitions $\{X_1,\dots,X_r\}$, $r \in \mathbb{N}$, of the particle label set $\{1,\dots,N\}$:

$$Z_\Lambda(\beta, N) = \frac{|\Lambda|^N}{N!} \sum_{\{X_1,\dots,X_r\}} \zeta_\Lambda(X_1) \cdots \zeta_\Lambda(X_r).$$

Monomers ($|X| = 1$) have activity 1, sets with higher cardinality have activity

$$|X| = k \geq 2: \ \zeta_\Lambda(X) = \frac{1}{|\Lambda|^k} \sum_{\gamma \in \mathcal{G}_{\mathrm{c}}(k)} \int_{\Lambda^k} \prod_{(ij)\in\gamma} f_{ij}(\boldsymbol{x}) \mathrm{d}x_1 \cdots \mathrm{d}x_k,$$

with $\mathcal{G}_{\mathrm{c}}(k)$ is the set of connected graphs with vertices $1,\dots,k$. Note that as $|\Lambda| \to \infty$, for every fixed k and β, the activity is related to the Mayer coefficients as follows:

$$|X| = k: \quad \zeta_\Lambda(X) \sim \frac{k!}{|\Lambda|^{k-1}}\, b_k(\beta) = \frac{B_k(\beta)}{|\Lambda|^{k-1}}$$

The formalism of cluster expansions for polymer partition functions gives

$$\log Z_\Lambda(\beta, N) = \log \frac{|\Lambda|^N}{N!} + \sum_{r\geq 1} \frac{1}{r!} \sum_{\substack{X=(X_1,\dots,X_r)\\ \text{conn},\ X_i\in\Gamma_N}} n(X)\, \zeta_\Lambda(X_1)\cdots\zeta_\Lambda(X_r).$$

Here Γ_N is the collection of subsets of $\{1,\dots,N\}$ of cardinality at least 2, and connectedness and $n(X)$ are defined as follows: With $X = (X_1,\dots,X_r) \in \Gamma_N^r$ we associate the graph $G(X)$ with vertices $1,\dots,r$ and edges $\{i,j\}$, $i \neq j$, $X_i \cap X_j \neq \emptyset$. The polymer X is called connected if the graph of overlaps $G(X)$ is, and $n(X) \in \mathbb{N}_0$ is the index of $G(X)$, i.e., $n(X) = n_+(X) - n_-(X)$ with $n_\pm(X)$ the number of connected subgraphs of $G(X)$ with an even (odd) number of edges.

The N-dependence in the summation index is slightly inconvenient. We remove it by exploiting the invariance with respect to particle relabeling,

$$\log Z_\Lambda(\beta, N) = \log \frac{|\Lambda|^N}{N!} + \sum_{n=2}^{N} \binom{N}{n} \sum_{r=1}^{\infty} \frac{1}{r!} \sum_{\substack{X=(X_1,\dots,X_r)\\ \text{conn},\ X_i\in\Gamma_n}} n(X) \\ \times \zeta_\Lambda(X_1)\cdots\zeta_\Lambda(X_r)\, \mathbf{1}\big(\cup_1^r X_i = \{1,\dots,n\}\big).$$

In the thermodynamic limit $N, |\Lambda| \to \infty$, for each cluster $X = (X_1,\dots,X_r)$ in the sum,

$$\frac{1}{|\Lambda|}\binom{N}{n} \zeta_\Lambda(X_1)\cdots\zeta_\Lambda(X_r) \sim \frac{1}{n!} \frac{N^n}{|\Lambda|^{1+\sum_1^r(|k_i|-1)}} \\ \times B_{k_1}(\beta)\cdots B_{k_r}(\beta), \quad k_i = |X_i|.$$

This goes to zero unless $1 + \sum_1^r (k_i - 1) = n$ (note that "$\geq$" for every cluster X). When this condition is satisfied, the overlap graph $G(X)$ is necessarily a tree, with index $n(X) = (-1)^{r-1}$, and the components are distinct, $X_i \neq X_j$. Assuming we can exchange summation and thermodynamic limits, we obtain

$$\begin{aligned} -\beta f(\beta,\rho) = -\rho(\log\rho - 1) &+ \sum_{n=2}^{\infty} \frac{\rho^n}{n!} B_n(\beta) \\ &+ \sum_{n=2}^{\infty} \frac{\rho^n}{n!} \sum_{r\geq 2} (-1)^{r-1} \sideset{}{^{(n)}}\sum_{\{X_1,\dots,X_r\}} \prod_{i=1}^{r} B_{|X_i|}(\beta). \end{aligned} \tag{40}$$

The sum $\sum^{(n)}$ is over collections of subsets $\{X_1,\dots,X_r\}$ with $(X_1,\dots,X_r)$ connected, $|X_i| \geq 2$ for all i, and such that $\cup_1^r X_i = \{1,\dots,n\}$ and $n = 1 + \sum_1^r (k_i - 1)$, and we recognize the coefficients given in (29).

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